Optimizing co-sintering of ceramic components for manufacturing of all-solid-state batteries

2020 Vehicle Technologies Office Annual Merit Review

June 2020

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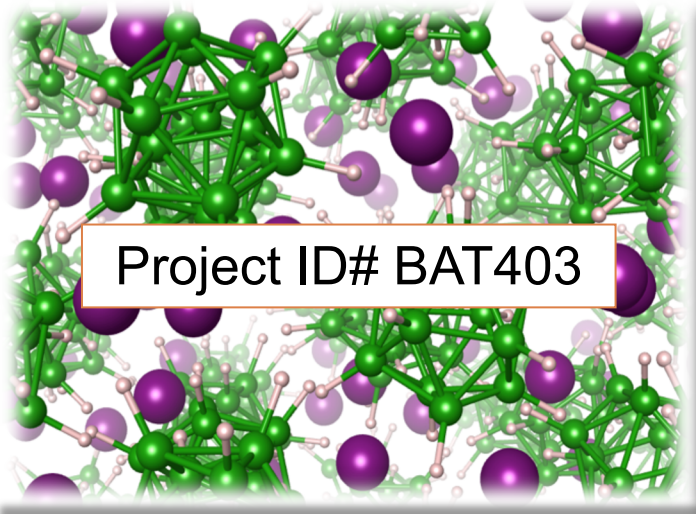
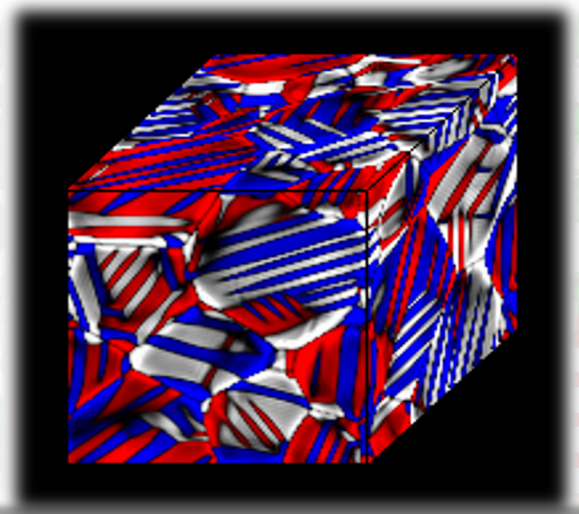
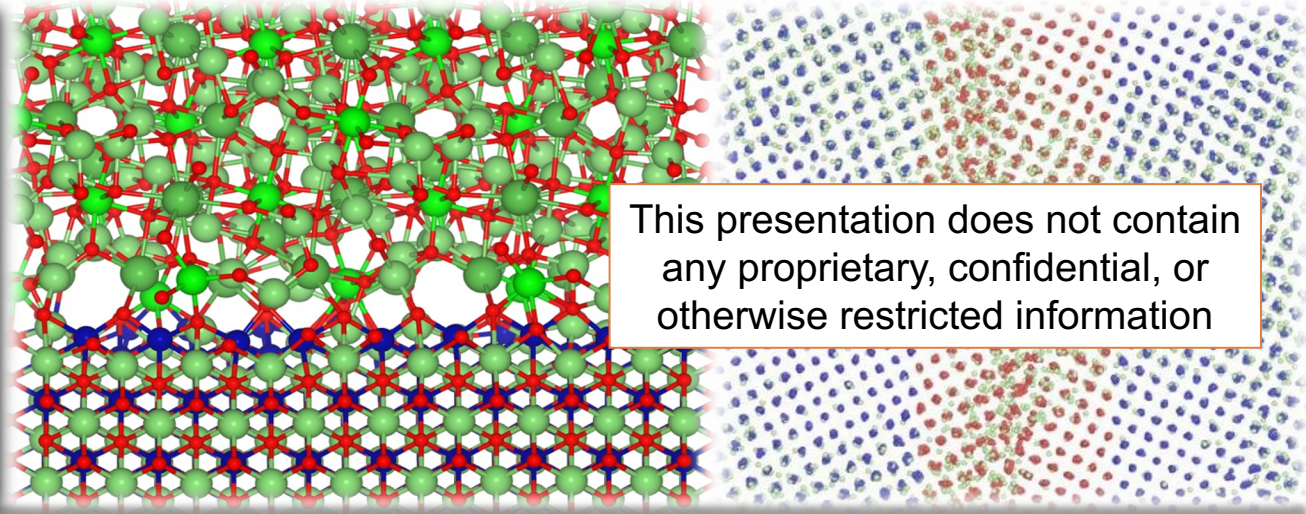


Project ID# BAT403





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LLNL-PRES-XXXXXX

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344. Lawrence Livermore National Security, LLC

Lawrence Livermore National Laboratory

Overview

Timeline

Project start date: 4/1/2019

Project end date: 9/30/2020

Barriers addressed

- **Cost (Barrier A):** Low-cost additives for lowering sintering temperatures
- **Performance (Barrier B):** Maintaining low impedance upon co-sintering of ceramic electrolyte and cathode

Budget

Total project funding: $300K (DOE share)

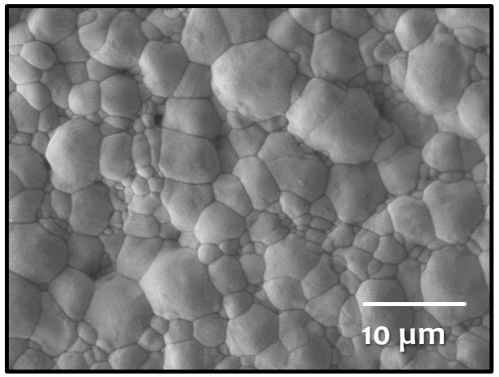
FY20 funding: $150K

Partners

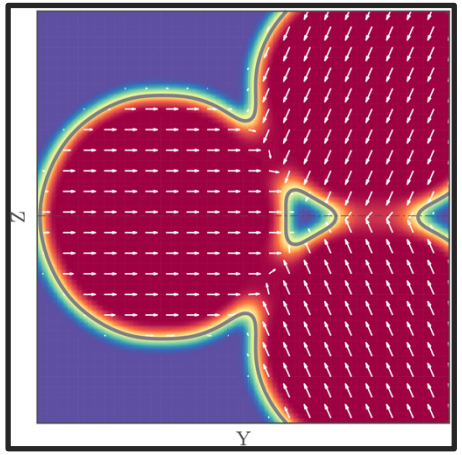
N/A

Relevance: Enabling reliable co-sintering of electrolytes and electrodes in ceramic solid-state batteries

- **Motivation:**
  - Ceramic solid-state batteries suffer from high interfacial impedance due to poor physical contacts between components
- **Problem:**
  - Although co-sintering can improve the physical contacts, the considerably higher sintering temperature for the electrolyte compared to the cathode leads to loss of cathode integrity
- **Need:**
  - Need new strategies to enable co-sintering at a lower temperature

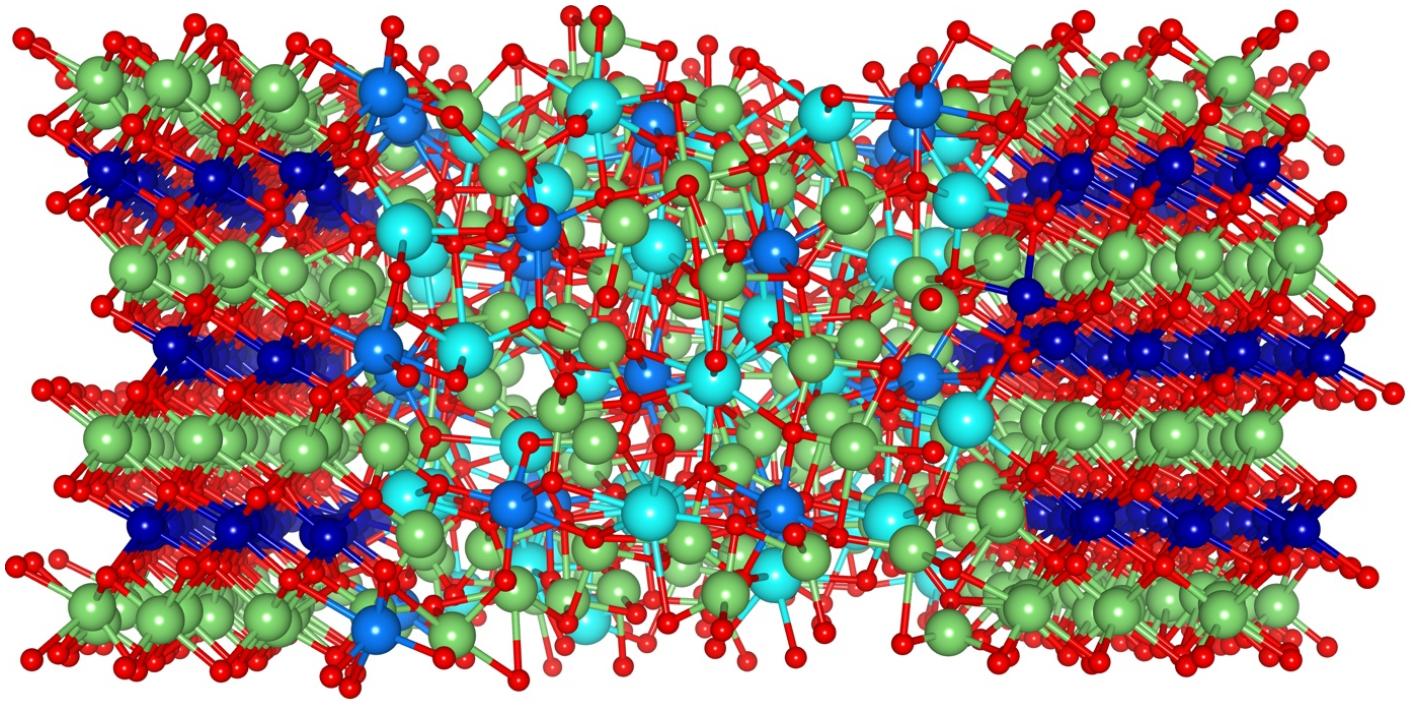


(Courtesy of Marissa Wood & Jianchao Ye, LLNL)



Relevance: Understanding key chemical and microstructural factors that determine electrolyte sintering temperature

Reducing sintering temperature of LLZO should lead to better interface contact, enhanced performance, and improved cyclability



Original goal: Use advanced modeling to determine if dilute chemical doping may lower the sintering temperature of LLZO while preserving integrity and performance

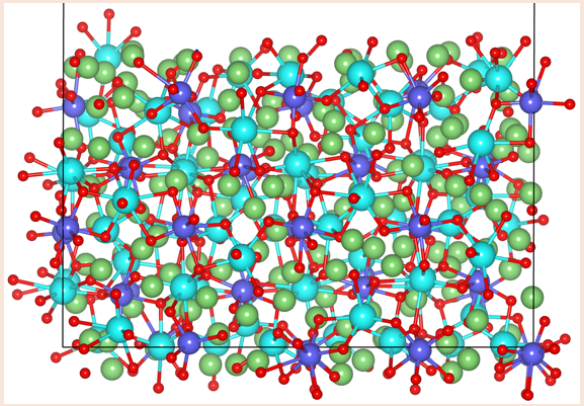
Secondary (stretch) goal added in FY20: Explore effects of particle size and microstructure on sintering temperature

Approach: Predicting and optimizing chemistry & microstructure

We leverage HPC resources and multiscale simulations to assess effects of dilute dopants and microstructure on sintering temperature

Chemistry

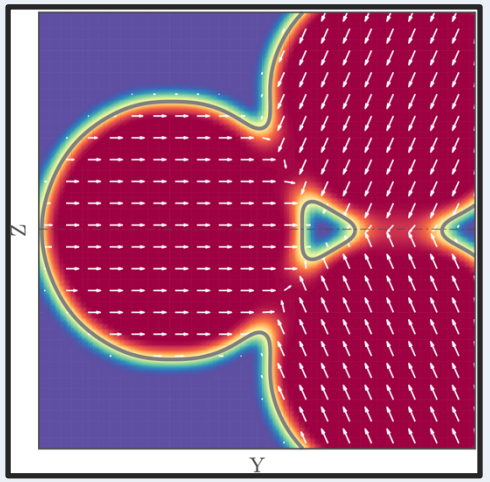
Quantum molecular dynamics



- Determine **proxy quantities** from simulations that can predict sintering temperature with composition
- **Calibrate** against experiments on baseline compositions

Microstructure

Mesoscale phase-field simulations



- Develop **direct sintering model** to probe effects of particle size and shape on sintering temperature
- Added as pilot effort in FY20

Quarterly milestones

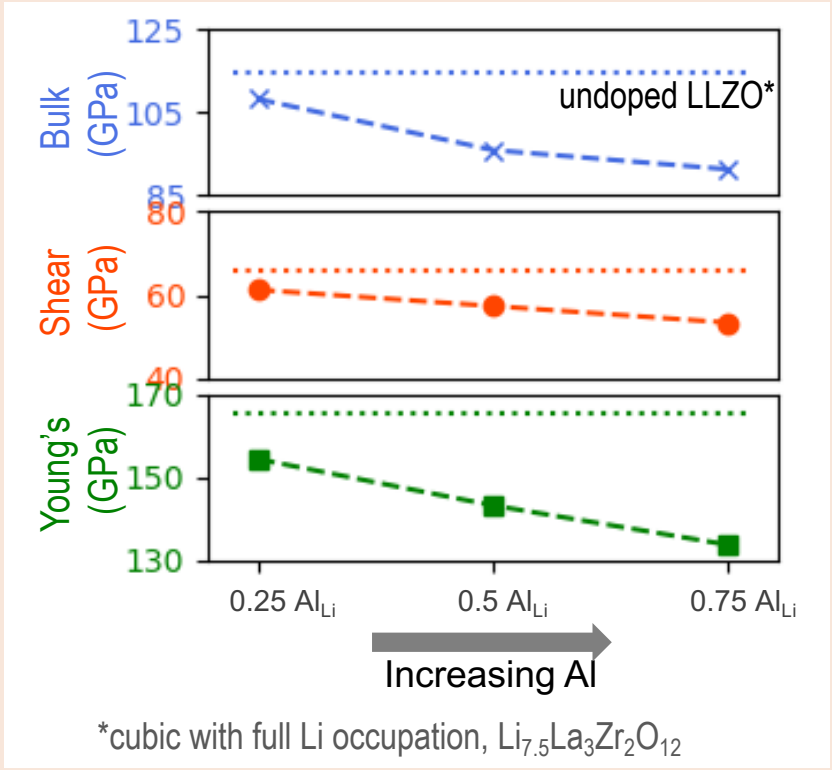
- **FY19Q2:** Compute bulk and shear modulus descriptors of doped LLZO for single concentration (100% complete)
- **FY19Q3 (adjusted):** Compute temperature for onset of surface premelting of doped LLZO for single concentration (adjusted to use structural reorganization as a proxy; 100% complete)
- **FY19Q4 (adjusted):** Compute bulk melting of doped LLZO for single concentration (adjusted to use premelting via Lindemann criterion; 100% complete)
- ***FY20Q1: Go/No-Go: Show that dopants are predicted to lower sintering temperature by > 100 °C compared with undoped LLZO* (delayed)***
- **FY20Q2:** For best descriptors, compute effects on sintering for multiple compositions (in progress; 50% complete)
- **FY20Q3 (adjusted):** Demonstrate mesoscale sintering model as a function of LLZO particle size (in progress; 80% complete)

Note: FY20 Go/No-Go delayed due to lack of access to experiments for calibration (currently working on mitigation strategy)

Accomplishment: Evaluation of static descriptors for composition-dependent sintering temperature

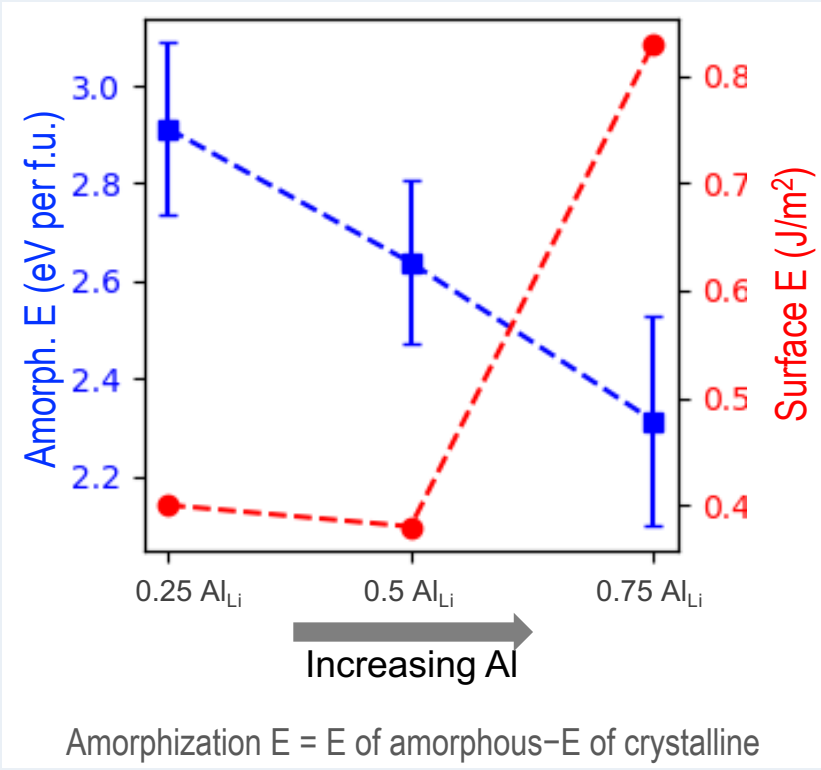
Tested elastic moduli, amorphization energy, and surface energy as static descriptors for sintering by assessing sensitivity to Al dopant concentration in model compositions

Moduli test mechanical hardness



*cubic with full Li occupation, $Li_{7.5}La_3Zr_2O_{12}$

Amorphization and surface energy test energy of perturbation



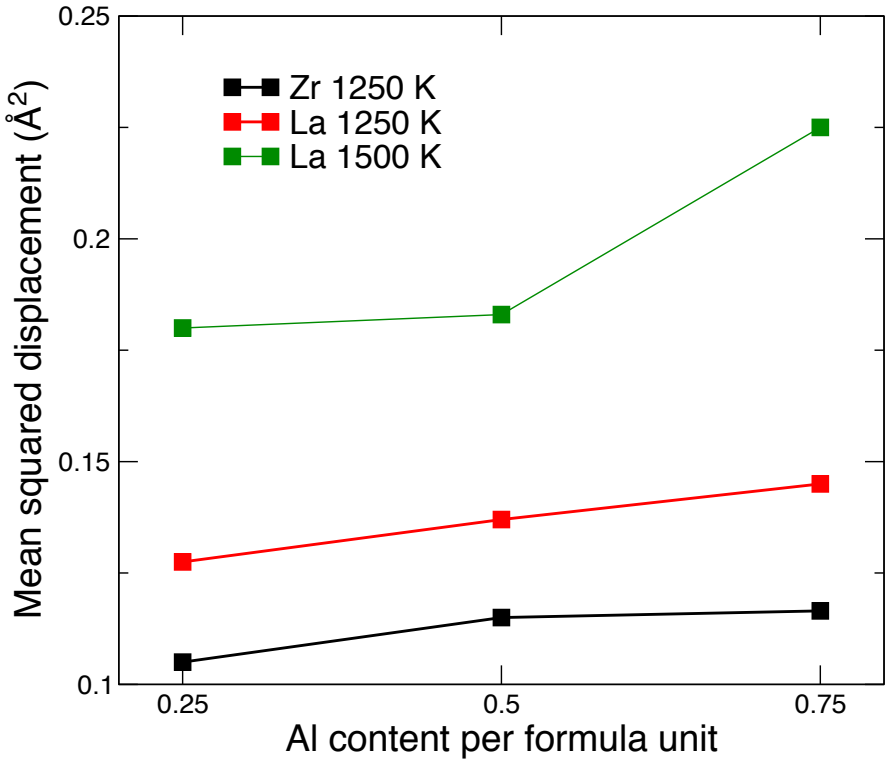
Amorphization E = E of amorphous−E of crystalline

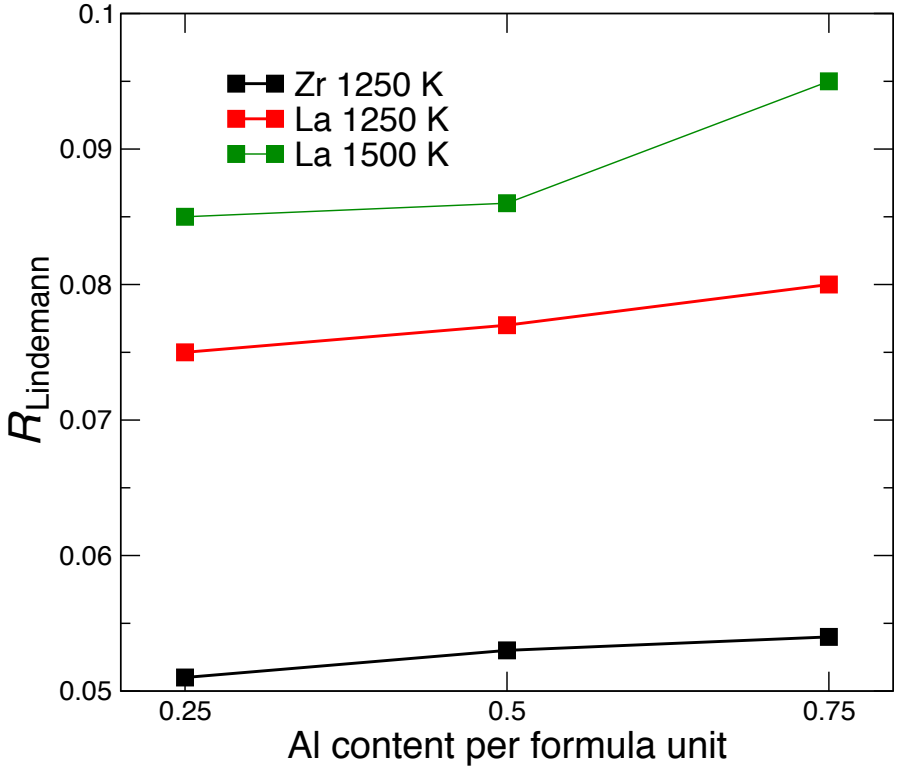
Elastic moduli and amorphization energy show consistent trend with Al doping and reasonable sensitivity; surface energy alone appears insufficient as a descriptor

Accomplishment: Evaluation of dynamic descriptors for composition-dependent sintering temperature: Lattice mobility

Tested La and Zr mean squared displacements (MSD) and their correlation to sintering/melting temperature via the empirical "Lindemann criterion"

Lindemann Criterion: Melting occurs when $R_{\text{Lindemann}} = \frac{\sqrt{\text{MSD}}}{\text{d}_{\text{interparticle}}} > 0.1$



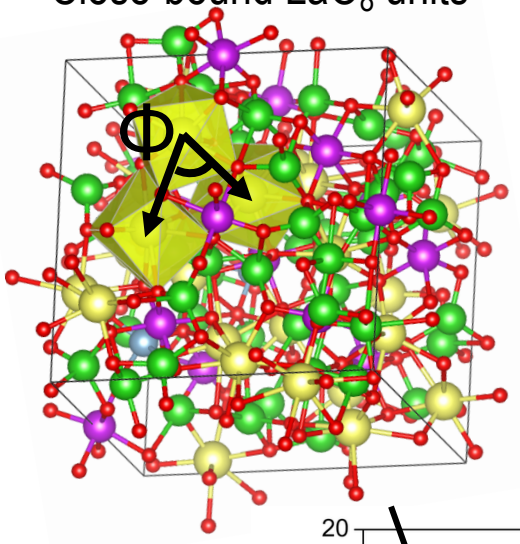


Zr MSD is a poor descriptor due to the stability of ZrO_6 octahedra, but La MSD shows promise in agreement with static descriptors, particularly at higher temperatures

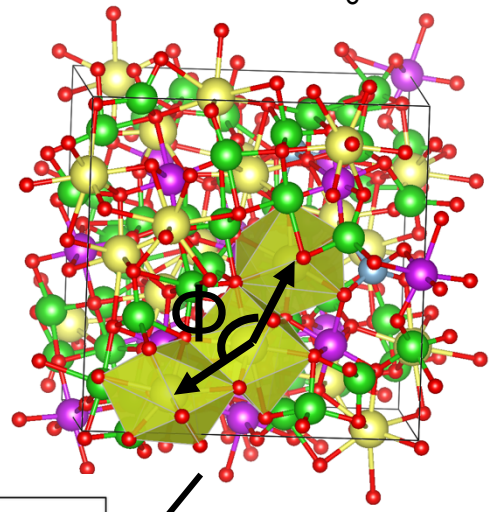
Accomplishment: Evaluation of dynamic descriptors for composition-dependent sintering temperature: Structural reorganization

Tested LaO_8 unit interconnectivity as a structural reorganization descriptor for sintering

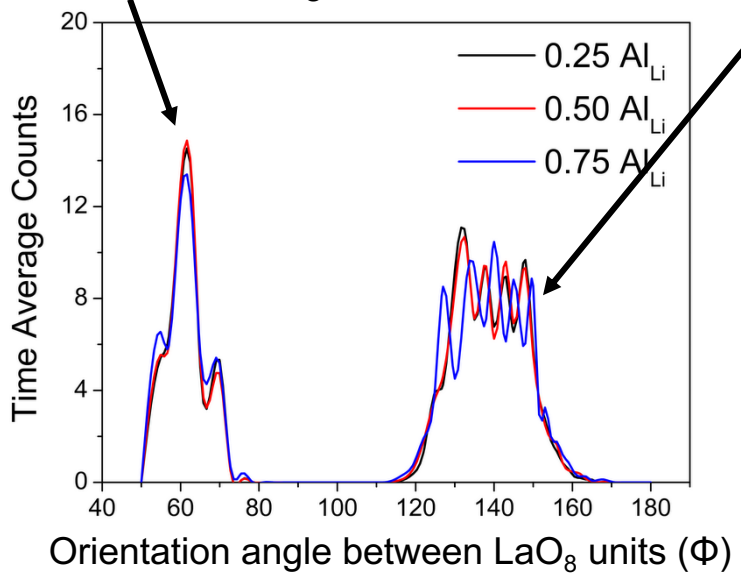
Close-bound LaO_8 units



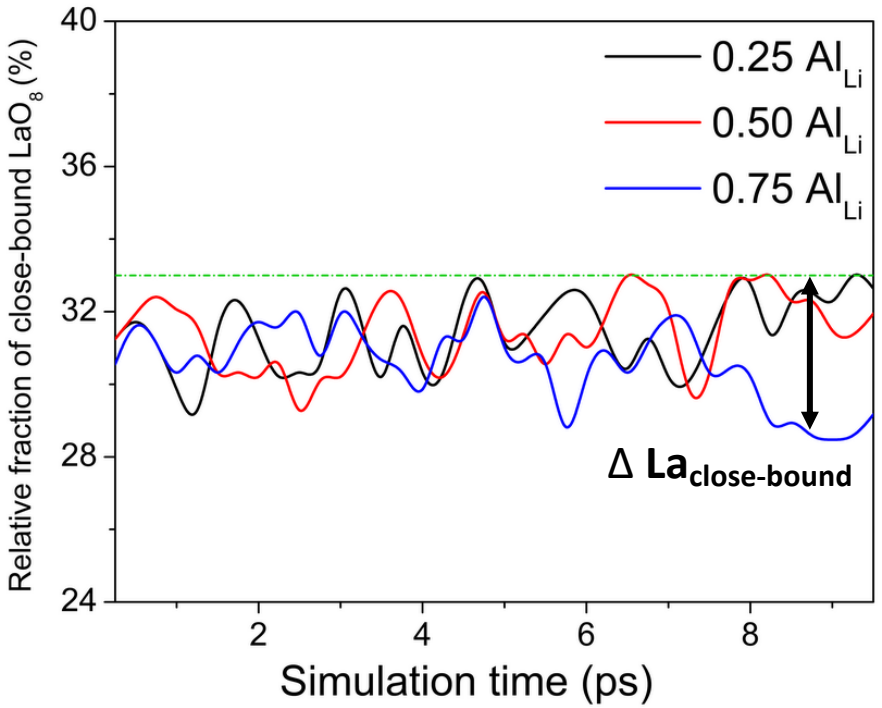
Chain-like LaO_8 units



Time average angle distribution



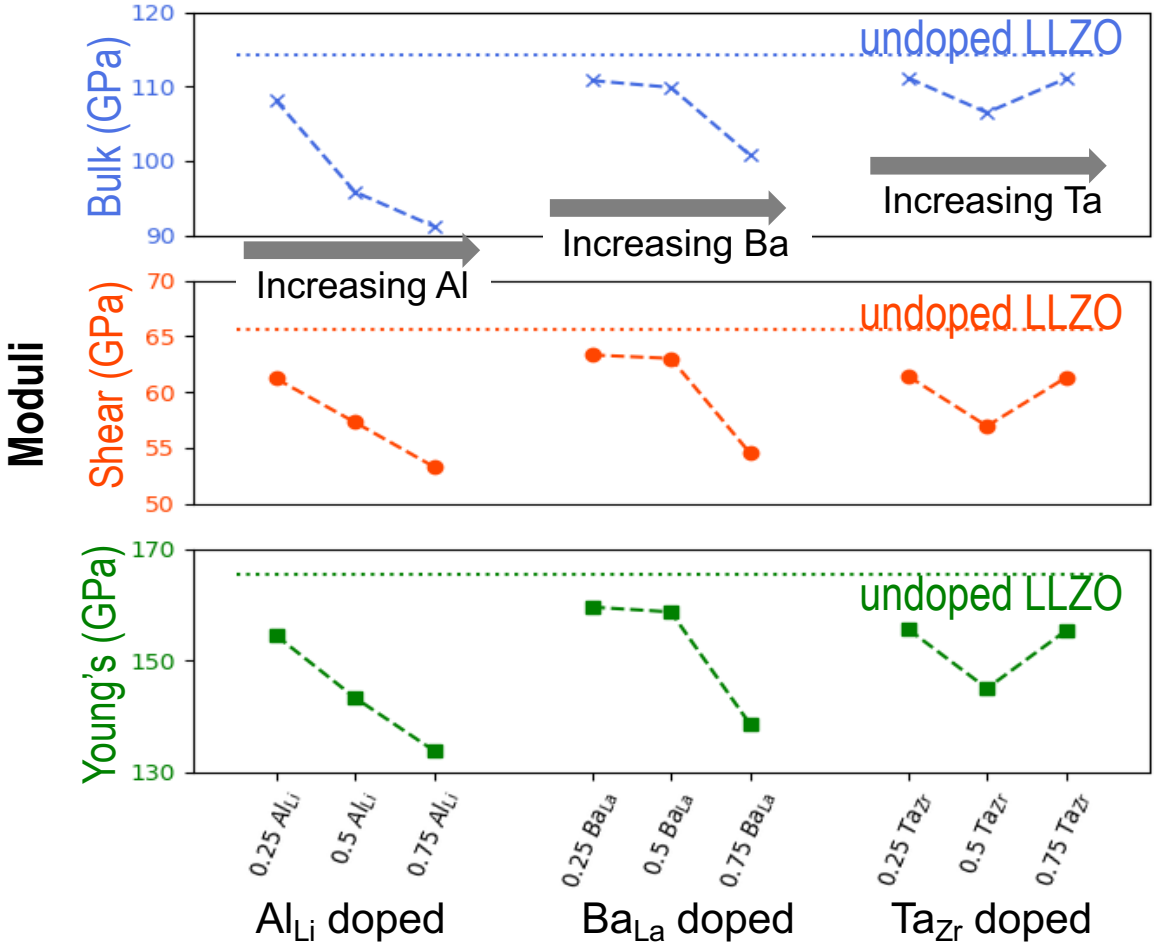
Time evolution of close-bound LaO_8 units



Decrease in relative fraction of LaO_8 close-bound units signals opening of structure that appears to correlate to sintering temperature

Accomplishment: Examining effects of substitutional doping of other atomic species

We selected other possible dopants (aliovalent Ba_{La}, Ta_{Zr}) based on computed energies as a first step to acquiring a broader set of data for experimental validation

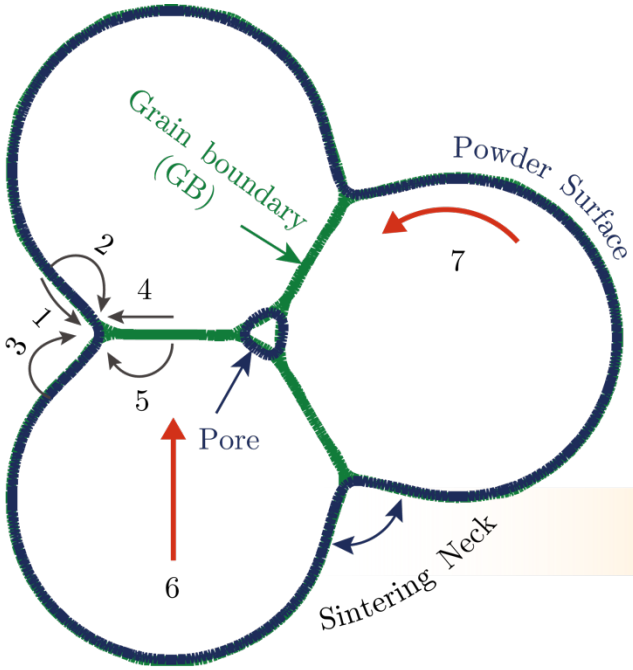


- Computation of **other proxy quantities** are currently in progress
- Plan to **calibrate against experiments** for doping level and role of dopants

Once descriptors are calibrated against experiments, we can explore the periodic table for dilute dopant combinations that can lower sintering temperature

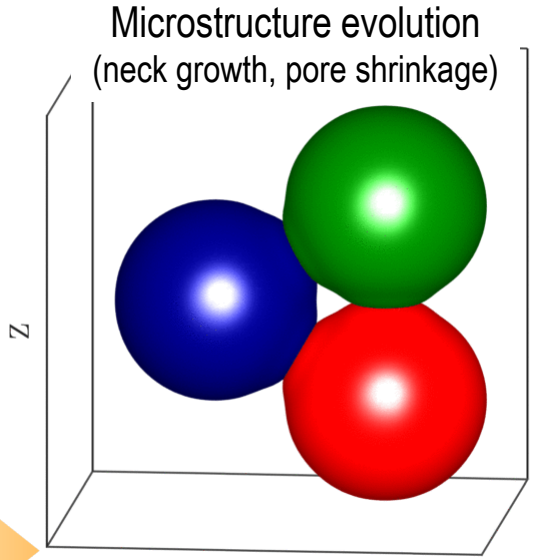
Accomplishment: Phase-field model includes impacts of mass transport mechanisms on densification kinetics in model microstructures

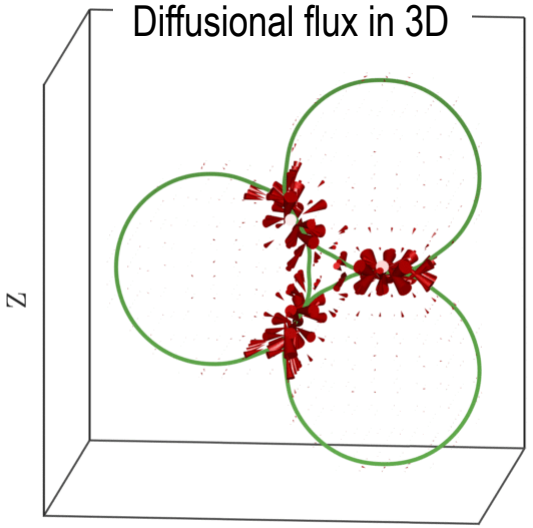
Developed mesoscale model of sintering and microstructure evolution that incorporates interaction of several physical mass transport mechanisms

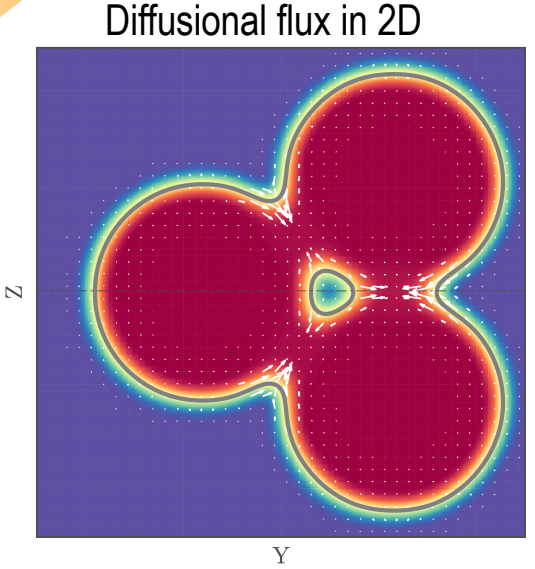


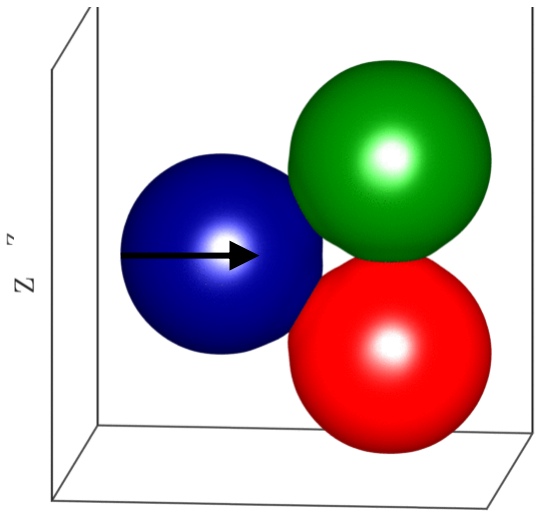
Model includes:

1. *Surface diffusion*
2. *Lattice diffusion from surface*
3. *Vapor transport*
4. *Grain boundary (GB) diffusion*
5. *Lattice diffusion from GB*
6. *Rigid-body translation*
7. *Rigid-body rotation*



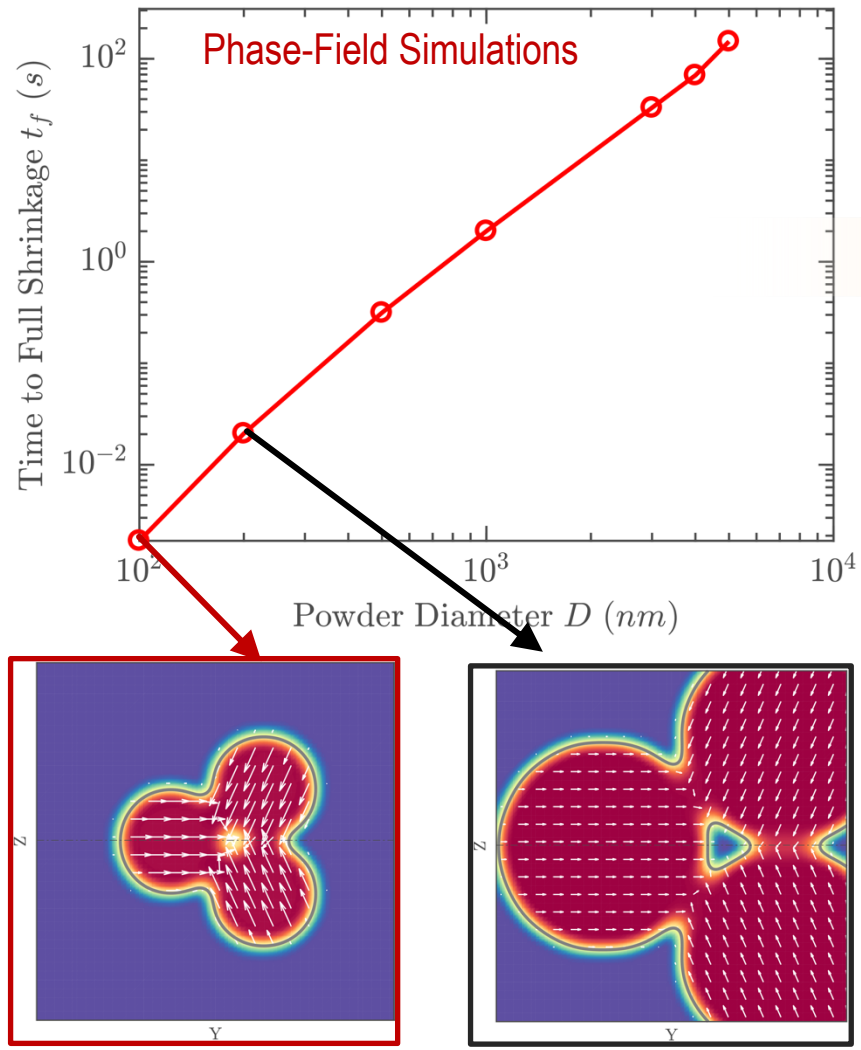






Accomplishment: First test on LLZO qualitatively predicts densification kinetics with powder size and elucidates primary underlying physics

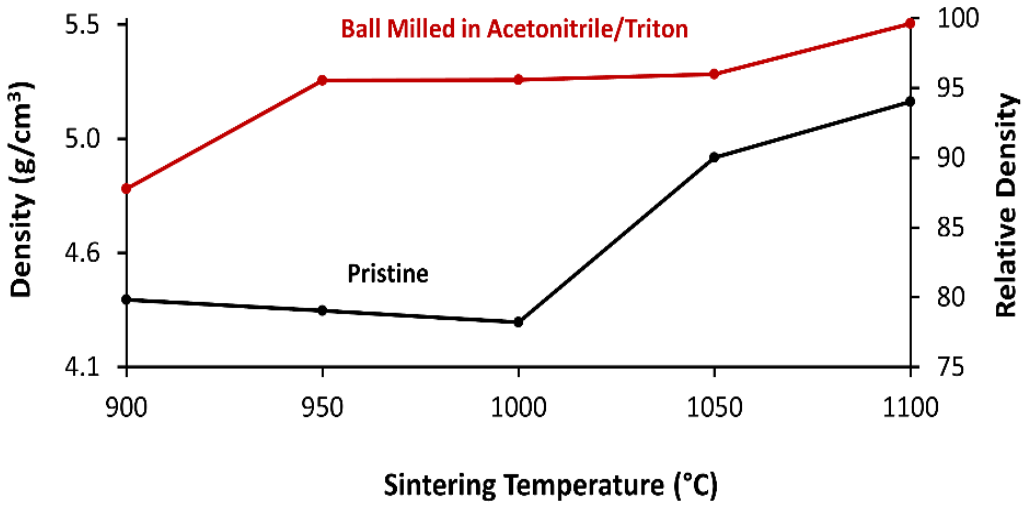
Successfully tested sintering model with general parameter set for oxides



Smaller particles show faster densification and reduced sintering temperature of LLZO due to:

1. Reduced volume of initial pores
2. Enhanced diffusional and advective flux

Experimental density of sintered pristine vs. high-energy ball milled LLZO (J. Ye & M. Wood, LLNL)



Preliminary results show trend in densification kinetics with particle size that matches collaborator experiments on pristine vs. ball-milled LLZO

Collaborations

Dr. Jianchao Ye, LLNL

- *Densification kinetics of pristine and ball-milled sintered LLZO samples*

Planned collaboration with Dr. Hyoungchul Kim, KIST (Korea)

- *Atomistic simulations of ceramic sintered solid electrolytes*

Remaining challenges & barriers

It is possible that no single descriptor is adequate for quantitatively predicting sintering temperature

- *We plan to pursue combinations of descriptors to improve predictive accuracy, but this requires enough compositions to assess universality*
- *To mitigate risk, we can rely on qualitative trends in our predicted proxy quantities*

Need reliable and controlled experimental validation data

- *Some early data has been obtained from internally funded effort and literature*
- *We are establishing links to other VTO program recipients for more detailed study*
- *Extension of scope to cover microstructure should help with this*

Beyond dilute chemical dopants, microstructure also plays a big role

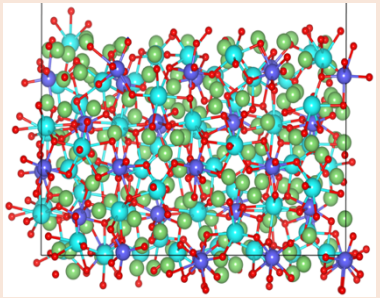
- *This year's extension of scope includes a promising pilot study to cover microstructure; however, further parameterization is required*

Publications & presentations

- L.F. Wan, A. Dive, M. Wood, T. Li, and B.C. Wood, “Integrated experiment-theory approach towards understanding complex interfacial chemistry in solid-state batteries,” ECS Meeting, Atlanta, GA (October 2019)

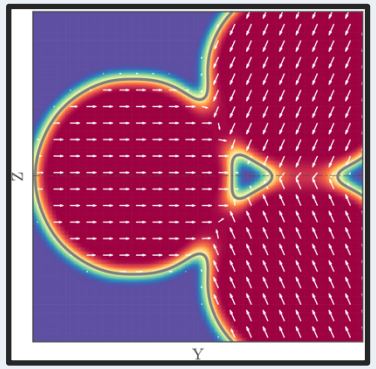
Proposed future work

Chemistry



- Complete testing of descriptors based on local structural dynamics
- Select best descriptors to apply to systems with other dopants
- Develop strategy for experimental calibration of sintering data
- Evaluate descriptor effectiveness and use to predict designability

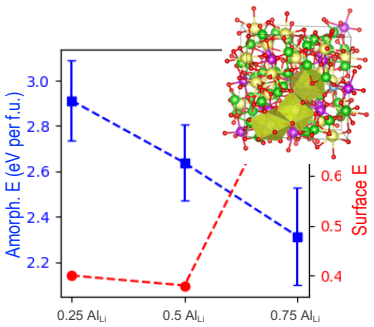
Microstructure



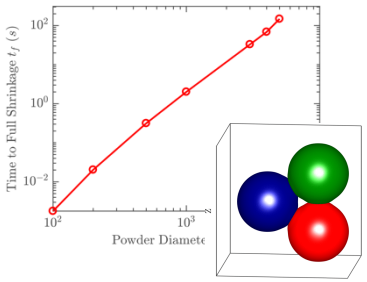
- Complete mesoscale sintering study as a function of particle size
- *Stretch goal: Parameterize sintering model with atomistic calculations**
- *Stretch goal: Use sintering model to investigate realistic particle geometries and define processing-microstructure relationships**

*Stretch goals subject to budgetary and future funding constraints

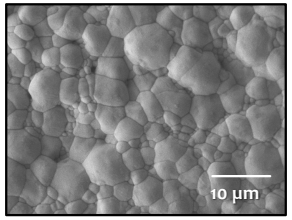
Summary



- We found multiple static and dynamic quantities that show sufficient sensitivity with Al composition to act as potential descriptors for LLZO sintering



- We started development on a new mesoscale sintering model for predicting densification kinetics upon changes in LLZO microstructure and particle packing



- Plan for experimental calibration and validation is underway